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High-pressure synthesis and characterization of the non-centrosymmetric scandium borate $\text{ScB}_6\text{O}_9(\text{OH})_3$

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Abstract: The non-centrosymmetric scandium borate $\text{ScB}_6\text{O}_9(\text{OH})_3$ was obtained through a high-pressure/high-temperature experiment at 6 GPa and 1473 K. Single-crystal X-ray diffraction revealed that the structure is isotypic to $\text{InB}_6\text{O}_9(\text{OH})_3$ containing borate triple layers separated by scandium layers. The compound crystallizes in the space group $Fdd2$ with the lattice parameters $a = 38.935(4)$, $b = 4.4136(4)$, and $c = 7.6342(6)$ Å. Powder X-ray diffraction and vibrational spectroscopy were used to further characterize the compound and verify the proposed structure solution.

Keywords: crystal structure; high-pressure chemistry; scandium borate; vibrational spectroscopy.

1 Introduction

Borates are a widely investigated substance class, due to their physical and chemical properties, which makes them interesting not only in the academical scope, but also for industrial applications. These properties mainly arise from the large number of crystal structures borates can adopt, based on their ability to form trigonal planar BO_3 groups as well as BO_4 tetrahedra. According to Bubnova and Filatov, more than 2400 borate crystal structures were listed in the ICSD database in 2013 [1], and this number has since been growing steadily.

During the past years, our group reinvestigated the broad field of transition metal borates with astounding

results. Through the use of high-pressure conditions for the syntheses, compounds with interesting structural properties could be realized, like $\text{HP-MB}_2\text{O}_4$ ($M = \text{Fe, Co, Ni}$) [2–4], the first borates, where every BO_4 tetrahedron shares one common edge with a second one, $\text{Cd}(\text{NH}_3)_2[\text{B}_3\text{O}_5(\text{NH}_3)]_2$ [5], the first ammine borate, or $\text{Mo}_2\text{B}_4\text{O}_9$ [6], which incorporates transition metal clusters into a borate framework. Despite these findings, there are many $M\text{-B-O}$ ($M = \text{transition metal}$) systems, where only very few compounds are known. For example, for the ternary system Sc-B-O , only three phases are known: ScBO_3 [7], $\text{Sc}_3\text{B}_5\text{O}_{12}$ [8], and $\text{Sc}_{1.67}\text{B}_3\text{O}_7$ [9]. While ScBO_3 is an ambient pressure compound, built up of layers of trigonal planar BO_3 groups, alternating with scandium layers, the latter two borates are high-pressure phases containing exclusively BO_4 tetrahedra. Interestingly, these two are also closely related to two natural occurring minerals. $\text{Sc}_3\text{B}_5\text{O}_{12}$ is homeotypic to the beryllo-silicate semenovite [10, 11], and $\text{Sc}_{1.67}\text{B}_3\text{O}_7$ represents the first ternary member of the melilite-type structure family [12].

In the present report, we present another high-pressure borate in the system Sc-B-O : $\text{ScB}_6\text{O}_9(\text{OH})_3$. It is isotypic to the indium borate $\text{InB}_6\text{O}_9(\text{OH})_3$ [13] and also represents the first non-centrosymmetric and the first hydroxylated scandium borate.

2 Results and discussion

2.1 Crystal structure

$\text{ScB}_6\text{O}_9(\text{OH})_3$ crystallizes with eight formula units ($Z = 8$) in the non-centrosymmetric orthorhombic space group $Fdd2$ (no. 43) with the lattice parameters $a = 38.935(4)$, $b = 4.4136(4)$, and $c = 7.6342(6)$ Å and a volume of $V = 1311.9(2)$ Å³. All relevant crystallographic and refinement data can be found in Table 1.

Like the already known isotypic compound $\text{InB}_6\text{O}_9(\text{OH})_3$ [13], the crystal structure is built up of triple layers of corner-sharing BO_4 tetrahedra, separated by scandium layers (Figure 1, middle). The BO_4 tetrahedra in the first and the third layer of these triples, with the

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Table 1: Crystal data and structure refinement of $\text{ScB}_6\text{O}_9(\text{OH})_3$.

Empirical formula	$\text{ScB}_6\text{O}_9(\text{OH})_3$
Molar mass, g mol^{-1}	304.84
Crystal system	orthorhombic
Space group	<i>Fdd2</i> (no. 43)
Single-crystal data	
<i>T</i> , K	183(2)
Radiation/wavelength λ , pm	$\text{MoK}\alpha/71.07$
<i>a</i> , Å	38.935(4)
<i>b</i> , Å	4.4136(4)
<i>c</i> , Å	7.6342(6)
<i>V</i> , Å ³	1311.9(2)
<i>Z</i>	8
Calculated density, g cm^{-3}	3.09
Absorption coeff., mm^{-1}	1.2
<i>F</i> (000), <i>e</i>	1200
Crystal size, mm^3	$0.110 \times 0.070 \times 0.020$
θ range, deg	2.1–35.1
Index ranges	$-62 \leq h \leq 59$ $-7 \leq k \leq 7$ $-12 \leq l \leq 12$
Reflections collected	8536
Independent reflections	1439
<i>R</i> _{int} / <i>R</i> _σ	0.0293/0.0232
Completeness to $\theta = 25.2^\circ$, %	100
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1349/1/105
Final <i>R</i> 1/ <i>wR</i> 2 indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0246/0.0702
Final <i>R</i> 1/ <i>wR</i> 2 indices (all data)	0.0298/0.0859
Goodness-of-fit on <i>F</i> ²	1.240
Flack parameter	0.02(2)
Largest diff. peak/hole, $e \text{ Å}^{-3}$	0.91/−0.93
Powder diffraction data	
Radiation/wavelength λ , pm	$\text{MoK}\alpha_1/70.93$
<i>a</i> , Å	38.928(5)
<i>b</i> , Å	4.4187(3)
<i>c</i> , Å	7.6418(5)
<i>V</i> , Å ³	1314.4(2)
2θ range, deg	2.0–42.0
2θ step width, deg	0.015
<i>R</i> _{exp} , %	2.17
<i>R</i> _{wp} , %	11.21
<i>R</i> _p , %	7.79

alternating central boron atoms B1 and B2, both form six-membered rings, where all the tetrahedra point towards the same direction (Figure 1, bottom left and right). In the first layer, this direction is $+a$, whereas in the third layer the orientation is changed to $-a$. The third layer is shifted by $1/4$ in the direction of b and $1/4$ in the direction of c , in relation to the first layer. Very similar six-membered rings can be found in other high-pressure borates, for example in CdB_2O_4 [14] and $\alpha\text{-FeB}_2\text{O}_4$ [15]. In contrast to $\text{ScB}_6\text{O}_9(\text{OH})_3$ presented here, where all BO_4 tetrahedra

show the same orientation in one layer – downwards (D) for the first and upwards (U) for the third layer – the sequences UDUDUD (for one-fourth of the six-membered rings) and UUUDDD are developed for the cadmium-compound, and UUDUDD for the iron-compound. In $\text{ScB}_6\text{O}_9(\text{OH})_3$, the layers of six-membered rings are connected via an intermediate layer, consisting of corrugated bands of BO_4 tetrahedra. In this middle layer, there are two half-occupied boron and the accompanying oxygen positions, designated as B3/B3a and O6/O6a, respectively, where only one is occupied at a time (Figure 1, bottom middle), leading to layers consisting exclusively either of B_3O_4 tetrahedra (light blue) or of B_3aO_4 tetrahedra (orange). The bands run in direction of $[0\bar{1}1]$ or $[01\bar{1}]$ for the tetrahedra with the central cation B3 and in direction of $[011]$ or $[0\bar{1}\bar{1}]$ for the tetrahedra with the central cation B3a (Figure 1, top). In contrast, the isotypic indium compound $\text{InB}_6\text{O}_9(\text{OH})_3$ [13] features only one fully occupied boron position in this layer, which is identical to the boron position B3 here. It is also within this middle layer, where we presume two hydrogen atoms to be bound to O6 and O6a. Due to the only half occupied positions, they could not be assigned in the refinement process, but this assumption coincides with the result for the isotypic $\text{InB}_6\text{O}_9(\text{OH})_3$ [13], where this position could be refined. This leads to two hydrogen atoms in the overall formula $M\text{B}_6\text{O}_9(\text{OH})_3$ ($M = \text{Sc}, \text{In}$), where the third one is postulated based on charge neutrality reasons.

Looking at the B–O bond lengths in this structure, a distinction can be made for the boron atoms B1 and B2, where the B–O distances lie within a much narrower range than for the only half-occupied atoms B3 and B3a. For the first two boron atoms, the average B–O distance is 1.471 Å, which is in good agreement with the literature (1.476(35) Å) [16]. In contrast, the overall average value of 1.466 Å is markedly shorter. A similar situation is found for the O–B–O angles. While the angles for the B_1O_4 and B_2O_4 tetrahedra vary only slightly, the angles for the tetrahedra with the half occupied central boron positions lie within a wider range of 104.8(7) to 113.6(8)°. Nevertheless, the average values of 109.4 and 109.5° match well with the expected tetrahedral angle. All the bond lengths and angles are listed in Tables 2 and 3, the atomic coordinates and isotropic displacement parameters are found in Table 4.

The scandium cations separate the triple layers and are positioned between the centres of two six-membered rings (Figure 2). Here, the upper layer is rotated about 180° compared to the lower layer, which is the reason for the very long a axis of 38.935(4) Å. Because of this rotation

Figure 1: Top: Different orientations of the disordered middle layer. Middle: Crystal structure of $\text{ScB}_6\text{O}_9(\text{OH})_3$ along $[010]$. Bottom (from left to right): First layer of six-membered rings pointing towards $+a$; second layer of either the light blue or the orange corrugated BO_4 chains (half occupied B3/B3a position); third layer of six-membered rings pointing towards $-a$.

Table 2: Interatomic B–O and Sc–O distances (Å) for $\text{ScB}_6\text{O}_9(\text{OH})_3$ (standard deviations in parentheses).

B1	–01	1.462(5)	B2	–05	1.467(3)	Sc1	–05	2.130(2)	2×
	–03	1.469(3)		–03	1.469(4)		–04	2.138(2)	2×
	–04	1.475(4)		–02	1.472(5)		–03	2.139(2)	2×
	–05	1.480(4)		–04	1.473(4)				
$\bar{d}$		1.472	$\bar{d}$		1.470	$\bar{d}$		2.136	
B3	–01	1.45(2)	B3a	–06a	1.42(2)				
	–06	1.447(8)		–01	1.46(1)				
	–06	1.48(2)		–06a	1.46(2)				
	–02	1.479(9)		–02	1.501(9)				
$\bar{d}$		1.46	$\bar{d}$		1.46				

of the triple layers against each other, four triple layers are needed to return to the initial position instead of two without the rotation. The Sc^{3+} cations between the anionic

triple layers are sixfold coordinated by oxygen atoms in an octahedral alignment. The Sc–O distances are in a narrow range of 2.130(2) to 2.139(2) Å, with an average

Table 3: Bond angles (deg) for $\text{ScB}_6\text{O}_9(\text{OH})_3$ (standard deviations in parentheses).

O5–B1–O3	107.8(3)	O4–B2–O3	108.0(2)
O5–B1–O4	108.5(2)	O5–B2–O4	108.7(2)
O4–B1–O3	108.9(2)	O3–B2–O2	109.2(2)
O4–B1–O1	110.2(2)	O5–B2–O2	109.6(2)
O3–B1–O1	110.4(2)	O5–B2–O3	110.0(2)
O5–B1–O1	111.1(2)	O4–B2–O2	111.3(2)
$\emptyset$	109.5	$\emptyset$	109.5
O6–B3–O2	104.9(6)	O2–B3a–O6a	104.8(7)
O6–B3–O1	106.2(7)	O2–B3a–O1	106.5(7)
O2–B3–O1	108.5(6)	O6a–B3a–O1	106.7(7)
O6–B3–O6	111.0(6)	O2–B3a–O6a	111.6(7)
O6–B3–O2	112.1(7)	O6a–B3a–O6a	112.9(8)
O6–B3–O1	113.5(7)	O1–B3a–O6a	113.6(8)
$\emptyset$	109.4	$\emptyset$	109.4

Table 4: Atomic coordinates and equivalent isotropic displacement parameters U_{eq} ($\text{\AA}^2$) of $\text{ScB}_6\text{O}_9(\text{OH})_3$. The Wyckoff positions are $8a$ for Sc1 and $16b$ for all other atoms.

Atom	s.o.f.	x	y	z	U_{eq}
Sc1	1	1/2	1/2	0.25263(9)	0.0031(2)
B1	1	0.5473(1)	0.5026(5)	0.5808(4)	0.0043(7)
B2	1	0.5470(1)	0.9946(6)	0.4164(4)	0.0030(6)
B3	0.5	0.6057(2)	0.778(2)	0.535(2)	0.005(2)
B3a	0.5	0.6065(3)	0.718(2)	0.476(2)	0.008(2)
O1	1	0.58484(7)	0.5196(4)	0.5828(3)	0.0089(5)
O2	1	0.58472(7)	0.9854(5)	0.4270(3)	0.0085(5)
O3	1	0.53245(5)	0.8056(4)	0.5564(2)	0.0035(3)
O4	1	0.53465(4)	0.3756(3)	0.7474(3)	0.0043(3)
O5	1	0.53508(5)	0.3082(4)	0.4357(2)	0.0038(3)
O6	0.5	0.6372(2)	0.809(2)	0.8615(7)	0.021(2)
O6a	0.5	0.6376(2)	0.696(2)	0.4489(7)	0.023(2)

distance of 2.136 Å. This distance is significantly shorter than in the two other known high-pressure scandium borates $\text{Sc}_3\text{B}_5\text{O}_{12}$ ($\emptyset$ Sc–O: 2.246 Å) [8] and $\text{Sc}_{1.76}\text{B}_3\text{O}_7$ ($\emptyset$ Sc–O: 2.244 Å) [9]. In these already known compounds, the scandium is coordinated by eight oxygen atoms in the form of distorted square antiprisms in contrast to the octahedral coordination in $\text{ScB}_6\text{O}_9(\text{OH})_3$. This sixfold coordination is related to the octahedral coordination of scandium in the ambient pressure compound ScBO_3 . Moreover, the Sc–O distance in this compound is 2.1200(4) Å, which is not far from the value derived from the crystal structure of $\text{ScB}_6\text{O}_9(\text{OH})_3$.

Corresponding to the increased In^{3+} cation size compared to Sc^{3+} , the cell parameters of the indium compound are slightly larger and also the B–O ($\emptyset$ = 1.489 Å) and In–O distances ($\emptyset$ = 2.177 Å) are longer than in the presented scandium compound [13]. Nevertheless, these

Figure 2: Octahedrally coordinated scandium position between the borate layers and in the middle of two six-membered rings. Sc–O distances in Å.

values are in good agreement with distances found in other high-pressure indium borates [17, 18].

The calculation of bond valence sums according to the bond length/bond strength (ΣV) concept [19, 20] reveals a more positive formal charge for O6 (ΣV = –1.55) and O6a (ΣV = –1.66), respectively, indicating a missing coordination, which agrees with the assumption that these two atoms are the bonding partners for two hydrogen atoms. The resulting formal ionic charges for the other atoms correspond well with the expected values within the limits of this concept and are shown in Table 5.

2.2 X-ray powder diffraction

The comparison between the experimental powder diffraction data and the pattern derived from the single-crystal refinement are depicted in Figure 3. Although $\text{ScB}_6\text{O}_9(\text{OH})_3$ is clearly the main reaction product, a certain amount of $\text{Sc}_3\text{B}_5\text{O}_{12}$ can be seen in the powder pattern, refined to a fraction of 10(1)%. Additionally, the difference curve suggests that at least one other unknown compound can be present. More details on the Rietveld refinement can be found in Table 1.

2.3 Vibrational spectroscopy

Figure 4 shows the IR spectrum of a $\text{ScB}_6\text{O}_9(\text{OH})_3$ powder sample in the range from 400 to 3800 cm^{-1} . The peak at

Table 5: Bond valence sums according to the bond length/bond strength (ΣV) concept.

	Sc1	B1	B2	B3	B3a	O1	O2	O3	O4	O5	O6	O6a
ΣV	+2.77	+3.05	+3.06	+3.11	+3.15	−2.38	−2.21	−1.99	−1.97	−1.98	−1.55	−1.66

Figure 3: Rietveld refinement of a $\text{ScB}_6\text{O}_9(\text{OH})_3$ sample, containing the side phase $\text{Sc}_3\text{B}_5\text{O}_{12}$. **Figure 4:** IR spectrum of a $\text{ScB}_6\text{O}_9(\text{OH})_3$ powder sample, also containing a certain amount of $\text{Sc}_3\text{B}_5\text{O}_{12}$.

around 3200 cm^{-1} can be attributed to stretching vibrations associated with the hydroxyl groups [21], thus confirming their existence in the structure. Even though the sample used for this measurement also contained a small amount of $\text{Sc}_3\text{B}_5\text{O}_{12}$, any contribution to the peak at the upper range of the spectrum can be ruled out, because this by-product

does not contain any hydrogen atoms. The tetrahedral BO_4 groups typically lead to the absorption bands in the range of $800\text{--}1150\text{ cm}^{-1}$ [22–24]. The broad absorption between ~ 1300 and 1500 cm^{-1} and the peaks below 800 cm^{-1} most likely originate from complex O–B–O, B–O–B, B–O, and Sc–B–O vibrations, which was confirmed by quantum mechanical calculations on $\beta\text{-ZnB}_4\text{O}_7$ and $\beta\text{-CaB}_4\text{O}_7$, two high pressure compounds with complex borate frameworks consisting of crystallographically independent BO_4 tetrahedra and O_3B groups [25].

3 Conclusion

$\text{ScB}_6\text{O}_9(\text{OH})_3$, representing the first non-centrosymmetric and the first hydroxylated scandium borate, was obtained at a pressure of 6 GPa and a temperature of 1473 K from scandium nitrate and boron oxide. Crystals of the compound are isotypic to the indium borate $\text{InB}_6\text{O}_9(\text{OH})_3$ and built up of anionic borate triple layers, the top and bottom ones forming six-membered rings and the middle one forming corrugated chains. They are separated by scandium layers in the bc plane, where the scandium atoms are octahedrally coordinated by oxygen atoms. The triple

layers are arranged in four slightly shifted orientations, resulting in a long unit cell with $a = 38.935(4)$ Å. Even though the hydrogen atoms could not be identified unambiguously in the crystal structure refinement, they were verified *via* vibrational spectroscopy.

4 Experimental section

4.1 Synthesis

The title compound $\text{ScB}_6\text{O}_9(\text{OH})_3$ was first obtained through a high-pressure/high-temperature experiment at 6 GPa and 1473 K. The synthesis was performed in an 18/11 assembly in a hydraulic 1000 t press with a modified Walker-type module (both Max Voggenreiter GmbH, Germany). $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%) and B_2O_3 (both Strem Chemicals, Inc., Newburyport, Massachusetts, USA, >99.9%) were grinded together in a stoichiometric ratio under ambient conditions and filled into a Pt capsule, which was placed in a crucible made of α -BN and closed with a lid of the same material (both Henze Boron Nitride Products AG, Germany). For a more detailed description of the experimental setup, the reader is referred to the literature [26–28].

The 18/11 assembly was compressed to 6 GPa within 150 min and heated to $T = 1473$ K in the following 10 min at a constant pressure. After keeping this temperature for the next 30 min, the sample was cooled to $T = 773$ K within another 180 min. Then, the sample was quenched to room temperature by switching off the heating and a 450 min decompression process was started. The recovered pressure medium was broken apart and the product carefully separated from the surrounding crucible and Pt capsule. A mixture of $\text{ScB}_6\text{O}_9(\text{OH})_3$ and $\text{Sc}_3\text{B}_5\text{O}_{12}$ appeared as colourless platelets.

4.2 Powder X-ray diffraction

A flat sample of the reaction product, containing $\text{ScB}_6\text{O}_9(\text{OH})_3$ and $\text{Sc}_3\text{B}_5\text{O}_{12}$, was characterized by powder diffraction analysis in transmission geometry on an STOE Stadi P powder diffractometer (STOE & Cie GmbH, Darmstadt, Germany) equipped with a Mythen 1K microstrip detector (Dectris). The measurement was carried out with Ge(111)-monochromatized $\text{MoK}\alpha_1$ radiation ($\lambda = 70.93$ pm) in the 2θ range of 2 – 52° with a step size of 0.015° . For a comparison with the values derived from the single-crystal structure analysis, a Rietveld refinement was performed employing the TOPAS 4.2 software [29].

4.3 Single-crystal X-ray analysis

The single-crystal structure determination was performed on a Bruker D8 Quest Kappa diffractometer with monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 71.07$ pm), equipped with an Incoatec microfocus X-ray tube and a Photon 100 CMOS detector. The structure solution and parameter refinement were performed with Direct Methods using SHELXS [30, 31] and the refinement against $|F_o|^2$ was carried out with SHELXL, both implemented in the WINGX software [32]. Despite measuring the crystal at $T = 183(2)$ K, it was not possible to unambiguously identify the position of the hydrogen atoms, also attributed to the half-occupied layer in which these atoms are expected to be found. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Further details of the crystal structure investigation of $\text{ScB}_6\text{O}_9(\text{OH})_3$ may be obtained from The Cambridge Crystallographic Data Centre CCDC/FIZ Karlsruhe deposition service via www.ccdc.cam.ac.uk/structures on quoting the deposition number CCDC 2000250.

4.4 Vibrational spectroscopy

For further characterization and to proof the existence of the postulated hydroxy groups in this compound, an FTIR-ATR (Attenuated Total Reflection) spectrum of a powder sample of $\text{ScB}_6\text{O}_9(\text{OH})_3$ was recorded. A Bruker ALPHA Platinum-ATR spectrometer (Bruker, Billerica, USA) with a 2×2 mm diamond ATR-crystal and a DTGS detector were used to collect the spectrum in the spectral range of 400 – 3800 cm^{-1} . A total of 320 scans of the powder sample were obtained and corrected for atmospheric influences afterwards, employing the OPUS 7.2 software [33].

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